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527 c'd PCT/PTO 03 MAY 2000

97P 8646P

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

09/530653

(REV 12-26-99)

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

INTERNATIONAL APPLICATION NO.  
PCT/DE98/03207INTERNATIONAL FILING DATE  
03/11/98PRIORITY DATE CLAIMED  
03/11/97

## TITLE OF INVENTION

Product, particularly of a gas turbine, with ceramic thermal barrier coat

## APPLICANT(S) FOR DO/EO/US

Beate Heimberg et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

- This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
- This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
- This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
- A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
- A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - is transmitted herewith (required only if not transmitted by the International Bureau).
  - has been transmitted by the International Bureau.
  - is not required, as the application was filed in the United States Receiving Office (RO/US).
- A translation of the International Application into English (35 U.S.C. 371(c)(2)).
- Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - are transmitted herewith (required only if not transmitted by the International Bureau).
  - have been transmitted by the International Bureau.
  - have not been made; however, the time limit for making such amendments has NOT expired.
  - have not been made and will not be made.
- A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
- An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
- A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11. to 16. below concern document(s) or information included:

- An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
- An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
- A **FIRST** preliminary amendment.
- A **SECOND** or **SUBSEQUENT** preliminary amendment.
- A substitute specification.
- A change of power of attorney and/or address letter.
- Other items or information:

17.  The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5) ) :**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$970.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$840.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$690.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)(4) ..... \$670.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$96.00

**ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 840.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than  20  30 months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	22	- 20 =	2
			X \$18.00
			\$ 36.00

Independent claims	3	- 3 =	0	X \$78.00	\$ 0.00
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MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$260.00	\$ 0.00
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**TOTAL OF ABOVE CALCULATIONS = \$876.00**

Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).

SUBTOTAL = \$ 876.00
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Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).
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<b>TOTAL NATIONAL FEE = \$ 876.00</b>
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Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property
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<b>TOTAL FEES ENCLOSED = \$ 876.00</b>
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Amount to be refunded: charged:	\$
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a.  A check in the amount of **\$ 876.00** to cover the above fees is enclosed.

b.  Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.

c.  The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-2556. A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

SIGNATURE:

Daniel C. Abeles

NAME

25,822

REGISTRATION NUMBER

09/530625

97P 8646P

526 Rec'd PCT/PTO 03 MAY 2000

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I hereby certify that this correspondence is being deposited with the United States Postal Service  
as first class mail in an envelope addressed to:

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BOX PCT

Washington, D.C. 20231, on 5-3-00

Jean Huckle  
Signature

5-3-00  
Date

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of )  
BEATE HEIMBERG et al. )  
Serial No.: Not Assigned Yet )  
Filed: May 3, 2000 )  
Entitled: ) Attorney Docket No.: 97P 8646P  
PRODUCT, PARTICULARLY COMPONENT )  
OF A GAS TURBINE, WITH CERAMIC )  
THERMAL BARRIER COATING )

Eckert Seamans Cherin & Mellott, LLC  
600 Grant Street, 44th Floor  
Pittsburgh, PA 15219

Assistant Commissioner for Patents  
BOX PCT  
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Please amend the above application as follows:

DISCLOSURE SHEET

In the specification:

- Page 1, line 1, cancel --Description--.
- Page 1, just above line 6, insert the heading "Field of the Invention".
- Page 1, just above line 13, insert the heading "Background".
- Page 4, just above line 19, insert the heading "Summary of the Invention".
- Page 4, line 28, cancel from the period through end of the paragraph on Page 5, line 7.
- Page 5, line 9, cancel --possible-- and insert "possibly".
- Page 6, cancel from line 16 through Page 10, line 20.
- Page 10, just above line 22, insert the heading "Brief Description of the Drawings".
- Page 10, just above line 29, insert the heading "Description of the Preferred Embodiment".
- Page 10, just below the heading "Description of the Preferred Embodiment" insert:

The invention is based on the finding that currently used ceramic thermal barrier coatings, despite the use of, e.g., partially stabilized zirconium oxide, have a thermal expansion coefficient which at maximum is only about 70% of the thermal expansion coefficient of the metallic basic body used, particularly of a superalloy. This lower thermal expansion coefficient of the zirconium oxide thermal barrier coatings compared to the metallic basic body causes thermal stresses during exposure to a hot gas. To counteract such resultant stresses occurring under alternating thermal stress, an expansion-tolerant microstructure of the thermal barrier coating is required, e.g., by adjusting a corresponding porosity or a columnar structure of the thermal barrier coating. In a zirconium oxide-based thermal barrier coating, continuous sintering of the coating material furthermore takes place during operation [missing verb] a change in the microstructure, disappearance of the porosity, occurrence of new defects or cracks, and possible failure of the thermal barrier coating in thermal and mechanical respects. In addition, in a thermal barrier coating of partially stabilized zirconium oxide by means of stabilizers such as yttrium oxide, cerium oxide or lanthanum oxide, stresses may occur that are created due to a thermally associated phase transition (tetragonal to monoclinic and cubic). Due to the associated volume change, a maximum permissible surface temperature for thermal barrier coatings made of zirconium oxide is given.

The use of a spinel provides a thermal barrier coating, possible taking into account mixed crystal formation and microstructure modification, with a high thermal expansion coefficient, low thermal conductivity, a high melting point, high chemical stability, a reduced tendency toward sintering, and a high phase stability.

According to the invention, the product-related object is attained in that the thermal barrier coating has a spinel of the composition  $AB_2X_4$ , where

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X represents oxygen, sulfur, selenium and/or tellurium. A represents an element or several elements of the group comprising aluminum, magnesium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, silicon, titanium and tungsten. B represents one or several elements of the group comprising aluminum, magnesium, manganese, iron, vanadium, chromium, gallium, silicon, titanium, sodium and potassium.

The thermal barrier coating is bonded to the basic body either directly or indirectly via a bond coat. Bonding is preferably effected via an oxide layer that is formed, for example, by oxidation of the basic body or of the bond coat. Bonding can also or additionally be effected through mechanical anchoring, e.g., through roughness of the basic body or the bond coat.

Such a thermal barrier coating particularly serves to prolong the life of products that are subjected to hot gas, e.g. gas turbine components, blades and heat shields. It exhibits low thermal conductivity, a high melting point, and is chemically inert.

It should be noted that the compound  $MgAl_2O_4$  (magnesium aluminate) is already frequently termed the spinel. The term spinel, as used in the invention, signifies the aforementioned group of compounds of the general formula  $AB_2X_4$ . The term "spinel" is intended to mean the so-called normal spinels ( $AB_2X_4$ ) as well as the "inverse" spinels ( $B(AB)_2X_4$ ). In addition to the conventional spinels, in which X represents oxygen, material systems where X represents selenium, tellurium or sulfur are also included. In the normal spinel type, the oxygen atoms form a nearly cubic-dense lattice, in the tetrahedral vacancies of which there are 8 A atoms and in the octahedral vacancies of which there are 16 B atoms. In contrast, in what is known as an inverse spinel, 8 B atoms are present in tetrahedral and the remaining 8 B atoms and the 8 A atoms in octahedral coordination.

Preferably, the product has a spinel with oxygen. Here, A represents a metallic element of valence  $2^+$  and B a metallic element of valence  $3^+$  (so-called 2-3 spinels). In this class of spinels, A represents preferably magnesium, iron, zinc, manganese, cobalt, nickel, titanium, copper or cadmium, and B represents aluminum, iron, chromium or vanadium.

Preferably, the spinel has aluminum or chromium as the B element and magnesium, nickel, or cobalt as the A element.

Furthermore, the thermal barrier coating preferably has a spinel in which B represents magnesium and A titanium.

In addition to the aforementioned 2-3 spinels with the valence  $A^{2+}$  and  $B^{3+}$ , there are other spinel types with a different valence of the cations, e.g., 1-6 spinels ( $WNa_2O_6$ ) and 2-4 spinels (e.g.  $Fe_2TiO_4$ ). In addition to the aforementioned elements that can represent the symbol A, aluminum, silicon, titanium and tungsten may also be used. B also comprises the elements magnesium, manganese, gallium, silicon, sodium and potassium.

The thermal conductivity of a preferred spinel is between 1.0 W/mK and 5.0 W/mK. The thermal expansion coefficient is preferably between  $6 \times 10^{-6} K$  and  $12 \times 10^{-6} K$  and the melting point is greater than  $1600^\circ C$ . The

indicated ranges for expansion coefficient and thermal conductivity apply to bodies of a ternary oxide with and "ideal" cell structure in manufacturing terms, i.e., without specifically introduced porosities. For  $MgAl_2O_4$ , e.g., the melting point is approximately  $2100^\circ C$ , thermal conductivity is  $4.0\text{ W/mK}$  at  $1945^\circ C$  and the thermal expansion coefficient is  $7.6$  to  $9.2 \times 10^{-6}/K$  at temperatures between  $25^\circ$  and  $1200^\circ C$ . For  $CoAl_2O_4$  the melting point is approximately  $1955^\circ C$  and the thermal expansion coefficient is between  $7$  and  $11 \times 10^{-6}/K$  at temperatures of between  $500^\circ$  and  $1500^\circ C$ . For  $MgCr_2O_4$  a melting point on the order of magnitude of  $2400^\circ C$  applies, a thermal expansion coefficient of between  $6.5$  and  $7.6 \times 10^{-6}/k$  at  $25^\circ$  to  $1200^\circ C$ , and a thermal conductivity [W/mK] of  $1.4$  in the range of  $25^\circ$  to  $300^\circ C$ . For  $CoCr_2O_4$  the melting point is above  $1600^\circ C$  and the thermal expansion coefficient is between  $7.5$  and  $8.5 \times 10^{-6}/K$  at  $500^\circ$  to  $1500^\circ C$ . The compound  $TiMg_2O_4$  has a melting point of  $1835^\circ C$  and a thermal expansion coefficient of  $6$  to  $12 \times 10^{-6}/K$  in the range of  $500^\circ$  to  $1500^\circ C$ .

Preferably, the spinel is present as a mixture in the ternary system of the type  $AB_2X_4$ - $AX$ - $B_2X_3$ . A metallic mixed oxide system with the spinel and an additional compound, particularly an oxide, may also be present. The spinel, or the spinel present as a mixture, can have an oxide or several oxides of the group comprising  $NiO$ ,  $CoO$ ,  $Al_2O_3$  and  $Cr_2O_3$ . This can be the case even if said oxides are not already a component of the spinel. In particular, said oxides can be present in an aluminite or a chromate spinel.

Furthermore, the spinel or a spinel consisting of a mixture can have an oxide or several oxides of the group comprising magnesium oxide ( $MgO$ ), zirconium oxide ( $ZrO_2$ ) and hafnium oxide ( $HfO_2$ ). This can be the case with spinels in which the oxides  $MgO$ ,  $ZrO_2$  and  $HfO_2$  are not already a component of the ternary system or the spinel, particularly with a chromate spinel or an aluminite spinel. A zirconium oxide or hafnium oxide present in the spinel is partially or fully stabilized particularly with yttrium oxide ( $Y_2O_3$ ) or another rare earth oxide. A rare earth metal is hereby understood to mean, for short, one of the elements scandium, yttrium, lanthanum, as well as the lanthanides such as cerium and ytterbium. Furthermore, oxides of the actinides may also be added.

The bond coat has preferably an alloy that comprises at least one element of the spinel. Hence, through at least partial oxidation of the bond coat, an oxide is formed of this element that is also contained in the spinel, e.g., aluminum, chromium, cobalt or others to provide good adhesion of the spinel to the bond coat. The bond coat is preferably an alloy of the type  $MCrAlY$ , where  $M$  represents an element or several elements of the group comprising iron, cobalt or nickel, Cr represents chromium, Al aluminum, and Y yttrium or a reactive rare earth element. Furthermore, the bond coat can include, e.g., 1 to 15 wt-% rhenium. The chromium content preferably ranges from 3% to 50%, particularly from 12% to 25%, the aluminum content is preferably between 3% and 20%, particularly between 5% and 15%. The yttrium content is preferably between 0.01% and 0.3%.

The product is preferably a component of a thermal turbo machine, particularly a gas turbine. In particular, it is a turbine moving blade, a turbine stationary blade, or a heat shield of a combustion chamber. The metallic basic body preferably has a nickel-, cobalt- and/or chromium based superalloy. It is also possible to provide a furnace or similar component with a thermal barrier coating made of a spinel.

The advantage of the spinels is their high tolerance to impurities, e.g., due to the formation of simple or complex mixed crystals in the presence of iron, aluminum, nickel, chromium or other metals, a good characterization of the sintering behavior of the high-melting spinels, and an essentially cubic structure and therefore quasi isotropic thermal expansion. Spinels furthermore exhibit good chemical resistance, high thermal shock resistance and high strength. Even with a transition of a spinel from its normal form to the inverse form, or at least partially to the inverse form, there are no abrupt changes in the physical-chemical properties. The transition from normal to inverse spinel can thus be considered an order-disorder induced phase transition of the second order, which has no great influence on the properties of the thermal barrier coating.

Thermal barrier coatings with a spinel may be produced, for example, by simple plasma spraying. A thermal barrier coating with a corresponding porosity can be produced by atmospheric plasma spraying. Alternatively, the thermal barrier coating may be applied by means of vapor deposition, e.g., an electron beam PVD process, with an adjustable columnar structure.

Preferably, the thermal barrier coating is applied by atmospheric plasma spraying, particularly with a predefinable porosity. The metallic mixed oxide system may also be applied by means of a suitable vapor deposition process, a suitable PVD process (Physical Vapor Deposition), particularly a reactive PVD process. When the thermal barrier coating is applied by means of vapor deposition, e.g., an electron beam PVD process, a columnar structure can be achieved if required. In a reactive PVD process, a reaction, particularly a conversion, of the individual components of a ternary oxide or a pseudo ternary oxide takes place only during the coating operation, particularly directly upon striking the product. In non-reactive vapor deposition, the previously pre-reacted products, particularly the ternary oxides with a perovskite structure are evaporated and are then deposited from the vapor onto the product. The use of pre-reacted products is advantageous particularly if plasma spraying is used.

The production (synthesis) of the spinels, e.g.,  $\text{NiCr}_2\text{O}_4$ ,  $\text{NiAl}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$  can be carried out phase-shift-free in the "mixed oxide process." In this case, the starting powders used are the associated binary oxides, e.g.,  $\text{Cr}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ . These powders can be homogenized under isopropanol, cold isostatically pressed, particularly at a pressure of 625 mPa, and subsequently tempered for 50 hours at  $1500^\circ \text{C}$  in air at a heat rate of 5 K/min.

Continue with the existing text as a separate paragraph, starting at Page 10, line 22.

In the claims:

Claim 5 (Amended) - Product (1) as claimed in [one of the preceding claims] Claim 2, characterized in that the spinel is present as a mixture in the ternary system of the type  $AB_2X_4$ - $AX$ - $B_2X_3$ .

Claim 6 (Amended) - Product (1) as claimed in [one of the preceding claims] Claim 2, characterized in that the mixed oxide system with the spinel has an additional oxide or several additional oxides.

Claim 7 (Amended) - Product (1) as claimed in [one of the preceding claims] Claim 6, characterized in that the additional oxide is stabilized with yttrium oxide ( $Y_2O_3$ ) or another rare earth oxide.

Claim 9 (Amended) - Product (1) as claimed in [one of the preceding claims] Claim 2, characterized in that between basic body (2) and thermal barrier coating (4) a bond coat (3) forming a bonding oxide is disposed.

Claim 11 (Amended) - Product (1) as claimed in [one of the preceding claims] Claim 2, characterized in that it is designed as a component of a thermal turbo machine, particularly a gas turbine.

Claim 13 (Amended) - Product (1) as claimed in [one of the preceding claims] Claim 2, characterized in that the thermal expansion coefficient  $\alpha$  of the spinel is between  $6 \times 10^{-6}/K$  and  $17 \times 10^{-6}/K$ .

Claim 14 (Amended) - Product (1) as claimed in [one of the preceding claims]

Claim 2, characterized in that the thermal conductivity of the spinel is between 1.0 W/mK and 4.0 W/mK.

Claim 15 (Amended) - Product (1) as claimed in [one of the preceding claims]

Claim 2, wherein the metallic basic body (4) has a nickel, cobalt and/or chromium-based super alloy.

Newly Added Claims

17. Product (1) as claimed in Claim 1, characterized in that the spinel is present as a mixture in the ternary system of the type  $AB_2X_4$ - $AX$ - $B_2X_3$ .

18. Product (1) as claimed in Claim 1, characterized in that the mixed oxide system with the spinel has an additional oxide or several additional oxides.

19. Product (1) as claimed in Claim 1, characterized in that between basic body (2) and thermal barrier coating (4) a bond coat (3) forming a bonding oxide is disposed.

20. Product (1) as claimed in Claim 1, characterized in that the thermal expansion coefficient  $\alpha$  of the spinel is between  $6 \times 10^{-6}/K$  and  $17 \times 10^{-6}/K$ .

21. Product (1) as claimed in Claim 1, characterized in that the thermal conductivity of the spinel is between 1.0 W/mK and 4.0 W/mK.

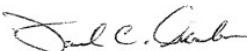
22. Product (1) as claimed in Claim 1, wherein the metallic basic body (4) has a nickel, cobalt and/or chromium-based super alloy.

In the abstract, Page 17, cancel line 11.

**REMARKS**

The foregoing amendments to the specification were made to conform to U.S. practice. The subject matter added to the description of the preferred embodiment can be found on Page 4 of the conformed copy of the translation starting at line 19. Accordingly, no new subject matter has been introduced by the foregoing amendments. The conformed copy of the translation has been formatted to facilitate an understanding of where the translated amendments, made during PCT prosecution, are to be inserted. Entry of this amendment and favorable consideration of the application are respectfully requested.

Respectfully submitted,



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5/21/04  
Date

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## Description

Product, Particularly Component of a Gas Turbine, with Ceramic Thermal Barrier Coating.

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The invention relates to a product that can be exposed to a hot aggressive gas, with a metallic basic body provided with a bond coat forming a bonding oxide and a ceramic thermal barrier coating. The invention furthermore relates to components that can be subjected to a hot gas in thermal machines, particularly in a gas turbine, 10 which are provided with a thermal barrier coating to protect them against a hot aggressive gas.

US Patent 4,585,481 discloses a protective coating to protect a metallic substrate made of a superalloy against high-temperate oxidation and corrosion. A MCrAlY 15 alloy is used for these protective coatings. This protective coating has 5% to 40% chromium, 8% to 35% aluminum, 0.1% to 2% of an oxygen active element selected from Group IIIb of the periodic system, including the lanthanides and actinides and mixtures thereof, 0.1% to 7% silicon, 0.1% to 3% hafnium, and a balance comprising nickel and/or cobalt (the percentages indicated are weight percent). The 20 corresponding MCrAlY alloy protective coatings according to US 4,585,481 are applied by plasma spraying.

US Patent 4,321,310 describes a gas turbine component with a basic body made of a nickel-based MAR-M-200 superalloy. A MCrAlY alloy layer is applied to the base 25 material, particularly a NiCOCrAlY alloy with 18% chromium, 23% cobalt, 12.5%

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GB 745 257 A discloses a process for coating a metal or another material with stable metal oxides. The other materials indicated, which may be used as a substrate for a coating, are ceramic materials and graphite. Various spinels, e.g., chromite  $\text{FeO} \bullet \text{Cr}_2\text{O}_3$ , chrysoberyl  $\text{BeO} \bullet \text{Al}_2\text{O}_3$ , gahnite  $\text{ZnAl}_2\text{O}_4$ , geikielite  $(\text{Mg}, \text{Fe})\text{O} \bullet \text{TiO}_2$  and  $\text{MgO} \bullet \text{Al}_2\text{O}_3$  (aluminate spinel) are applied as the coating material to the substrate by means of thermal spraying. With this process, the aforementioned minerals are sprayed, for example, onto the turbine blades of aircraft engines.

aluminum, 0.3% yttrium and a balance of nickel. This MCrAlY alloy layer has a polished surface to which an aluminum oxide layer is applied. A ceramic barrier coating with a columnar structure is applied to this aluminum oxide layer. Due to this columnar microstructure of the thermal barrier coating, the crystallite  
5 columns are perpendicular to the surface of the basic body. The ceramic material specified is stabilized zirconium oxide.

US Patent 5,236,787 discloses the insertion of an interlayer of a metal-ceramic mixture between the basic body and a ceramic thermal barrier coating. This is  
10 intended to cause the metallic proportion of this interlayer to increase toward the basic body and to decrease toward the thermal barrier coating. Conversely, the ceramic proportion is to be low near the basic body and high near the thermal barrier coating. The thermal barrier coating specified is a zirconium oxide stabilized with yttrium oxide with components of cerium oxide. With this interlayer an  
15 adaptation of the different thermal expansion coefficients between the metallic basic body and the ceramic thermal barrier coating is to be achieved.

EP 0 486 489 B1 discloses a corrosion resistant protective coating for intermediate and high temperatures of up to approximately 1050° C for a gas turbine component  
20 made of a nickel-base or cobalt-base alloy. The protective coating has (in percent by weight) 25% to 40% nickel, 28% to 32% chromium, 7% to 9% aluminum, 1% to 2% silicon, and 0.3% to 1% of at least one reactive rare earth element, at least 5% cobalt, and optionally 0% to 15% of at least one of the elements of the group consisting of rhenium, platinum, palladium, zirconium, manganese, tungsten,  
25 titanium, molybdenum, niobium, iron, hafnium and tantalum. In a concrete embodiment, the protective coating contains the elements nickel, chromium, aluminum, silicon, yttrium, and rhenium in a range of 1% to 15% and a balance of cobalt. The addition of rhenium clearly enhances the corrosion protective properties.

WO 96/34128 A1 discloses a product, particularly a gas turbine blade, with a metallic substrate. A protective coating system comprising a bond coat and a thermal barrier coating is applied to the metallic substrate. The thermal barrier coating consists of a columnar ceramic oxide, particularly made of a partially stabilized zirconium oxide. This thermal barrier coating is bonded to the metallic substrate via an anchoring layer. The anchoring layer in turn is bonded via the bond coat to the metallic substrate, particularly a nickel-based or cobalt-based superalloy. The bond coat consists of a MCrAlY alloy, such as indicated, for example, in US Patents 5,154,885; 5,268,238; 5,273,712, and 5,401,307. The anchoring layer for its part consists of a spinel comprising aluminum and an other metallic element. The other metallic element is preferably zirconium. The anchoring layer is preferably applied by means of a PVD process, particularly an electron beam PVD process, in an oxygen-containing atmosphere. During the coating operation, the metallic substrate is kept at a temperature of above 700° C. The thickness of the anchoring layer is preferably less than 25 µm.

WO 96/31293 A1 describes a protective coating system for a gas turbine blade that is applied to a superalloy component for protection. The protective coating system comprises a zirconium oxide-based thermal barrier coating. To this zirconium oxide-based thermal barrier coating, a wear coat is applied that is to prevent premature damage to the thermal barrier coating. Such premature wear of the unprotected thermal barrier coating occurs due to contact with a hot aggressive gas containing oxides of calcium or magnesium. The wear layer has a composition that reacts with the oxides in the hot aggressive gas, which increases the melting temperature and the viscosity of the wear layer. For this purpose, the wear layer comprises, for example, aluminum oxide, magnesium oxide, chromium oxide and a spinel, e.g., magnesium-aluminum oxide.

US Patent 5,466,280 (corresponding to GB 2 286 977 A1) discloses a composition  
30 for an inorganic coating applied to a low alloy steel and resistant to high  
temperatures. The predominant property of the coating is that it provides increased

corrosion resistance by incorporating iron into the coating. The coating is created by converting different metal oxides, such as magnesium oxide, aluminum oxide, iron oxide and calcium oxide at temperatures of above 1000° C into spinels, which are not further specified.

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German Application 15 83 971 discloses a refractory protective layer for metallurgical furnaces, which protective layer has a spinel, namely  $MgO-Al_2O_3$ . German Patent 37 37 215 discloses a protective coating containing spinel ( $MgO-Al_2O_3$ ) for an electrochemical sensor to determine the oxygen content in gases,

- 10 particularly exhaust gases of internal combustion engines of automobiles.

EP 0 684 322 A2 discloses a  $MgO - SiO_2$  and/or  $MgO - Al_2O_3$  based ceramic coating made particularly of forsterite ( $Mg_2SiO_4$ ), spinel ( $MgAl_2O_4$ ) or cordierites ( $2MgO - 2Al_2O_3 - 5SiO_3$ ).

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The object of the invention is to define a product, particularly a component of a gas turbine, with a metallic basic body and a thermal barrier coating disposed thereon.

- 20 The invention is based on the finding that currently used ceramic thermal barrier coatings, despite the use of, e.g., partially stabilized zirconium oxide, have a thermal expansion coefficient which at maximum is only about 70% of the thermal expansion coefficient of the metallic basic body used, particularly of a superalloy. This lower thermal expansion coefficient of the zirconium oxide thermal barrier coatings compared to the metallic basic body causes thermal stresses during
- 25 exposure to a hot gas. To counteract such resultant stresses occurring under alternating thermal stress, an expansion-tolerant microstructure of the thermal barrier coating is required, e.g., by adjusting a corresponding porosity or a columnar structure of the thermal barrier coating. In a zirconium oxide-based thermal barrier coating, continuous sintering of the coating material furthermore
- 30 takes place during operation [missing verb] a change in the microstructure, disappearance of the porosity, occurrence of new defects or cracks, and possible

failure of the thermal barrier coating in thermal and mechanical respects. In addition, in a thermal barrier coating of partially stabilized zirconium oxide by means of stabilizers such as yttrium oxide, cerium oxide or lanthanum oxide, stresses may occur that are created due to a thermally associated phase transition 5 (tetragonal to monoclinic and cubic). Due to the associated volume change, a maximum permissible surface temperature for thermal barrier coatings made of zirconium oxide is given.

The use of a spinel provides a thermal barrier coating, possibly taking into account 10 mixed crystal formation and microstructure modification, with a high thermal expansion coefficient, low thermal conductivity, a high melting point, high chemical stability, a reduced tendency toward sintering, and a high phase stability.

According to the invention, the product-related object is attained in that the thermal 15 barrier coating has a spinel of the composition  $AB_2X_4$ , where X represents oxygen, sulfur, selenium and/or tellurium. A represents an element or several elements of the group comprising aluminum,

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magnesium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, silicon, titanium and tungsten. B represents one or several elements of the group comprising aluminum, magnesium, manganese, iron, vanadium, chromium, gallium, silicon, titanium, sodium and potassium.

5

- The thermal barrier coating is bonded to the basic body either directly or indirectly via a bond coat. Bonding is preferably effected via an oxide layer that is formed, for example, by oxidation of the basic body or of the bond coat. Bonding can also or additionally be effected through mechanical anchoring, e.g., through roughness of 10 the basic body or the bond coat.

Such a thermal barrier coating particularly serves to prolong the life of products that are subjected to a hot gas, e.g. gas turbine components, blades and heat shields. It exhibits low thermal conductivity, a high melting point, and is chemically inert.

15

- It should be noted that the compound  $MgAl_2O_4$  (magnesium aluminate) is already frequently termed the spinel. The term spinel, as used in the invention, signifies the aforementioned group of compounds of the general formula  $AB_2X_4$ . The term "spinel" is intended to mean the so-called normal spinels ( $AB_2X_4$ ) as well as the 20 "inverse" spinels ( $B(AB)_2X_4$ ). In addition to the conventional spinels, in which X represents oxygen, material systems where X represents selenium, tellurium or sulfur are also included. In the normal spinel type, the oxygen atoms form a nearly cubic-dense lattice, in the tetrahedral vacancies of which there are 8 A atoms and in the octahedral vacancies of which there are 16 B atoms. In contrast, in what is 25 known as an inverse spinel, 8 B atoms are present in tetrahedral and the remaining 8 B atoms and the 8 A atoms in octahedral coordination.

- Preferably, the product has a spinel with oxygen. Here, A represents a metallic element of valence  $2^+$  and B a metallic element of valence  $3^+$  (so-called 2-3 spinels). In this class of spinels, A represents preferably magnesium, iron, zinc, manganese, cobalt, nickel, titanium, copper or cadmium, and B represents
- 5 aluminum, iron, chromium or vanadium.

Preferably, the spinel has aluminum or chromium as the B element and magnesium, nickel, or cobalt as the A element.

- 10 Furthermore, the thermal barrier coating preferably has a spinel in which B represents magnesium and A titanium.

- In addition to the aforementioned 2-3 spinels with the valence  $A^{2+}$  and  $B^{3+}$ , there are other spinel types with a different valence of the cations, e.g., 1-6 spinels
- 15 ( $WNa_2O_4$ ) and 2-4 spinels (e.g.  $Fe_2TiO_4$ ). In addition to the aforementioned elements that can represent the symbol A, aluminum, silicon, titanium and tungsten may also be used. B also comprises the elements magnesium, manganese, gallium, silicon, sodium and potassium.
- 20 The thermal conductivity of a preferred spinel is between 1.0 W/mK and 5.0 W/mK. The thermal expansion coefficient is preferably between  $6 \times 10^{-6}/K$  and  $12 \times 10^{-6}/K$  and the melting point is greater than  $1600^\circ C$ . The indicated ranges for expansion coefficient and thermal conductivity apply to bodies of a ternary oxide with an “ideal” cell structure in manufacturing terms, i.e., without specifically
- 25 introduced porosities. For  $MgAl_2O_4$ , e.g., the melting point is approximately  $2100^\circ C$ , thermal conductivity is 4.0 W/mK at  $1945^\circ C$  and the thermal expansion coefficient is  $7.6$  to  $9.2 \times 10^{-6}/K$  at temperatures between  $25^\circ$  and  $1200^\circ C$ . For  $CoAl_2O_4$  the melting point is approximately  $1955^\circ C$  and the thermal expansion coefficient is between  $7$  and  $11 \times 10^{-6}/K$  at temperatures of between  $500^\circ$  and  $1500^\circ$
- 30 C. For  $MgCr_2O_4$  a melting point on the order of magnitude of  $2400^\circ C$  applies, a thermal expansion coefficient of between  $6.5$  and  $7.6 \times 10^{-6}/K$  at  $25^\circ$  to  $1200^\circ C$ ,

and a thermal conductivity [W/mK] of 1.4 in the range of 25° to 300° C. For CoCr<sub>2</sub>O<sub>4</sub> the melting point is above 1600° C and the thermal expansion coefficient is between 7.5 and 8.5 x 10<sup>-6</sup>/K at 500° to 1500° C. The compound TiMg<sub>2</sub>O<sub>4</sub> has a melting point of 1835° C and a thermal expansion coefficient of 6 to 12 x 10<sup>-6</sup>/K in  
5 the range of 500° to 1500° C.

Preferably, the spinel is present as a mixture in the ternary system of the type AB<sub>2</sub>X<sub>4</sub>–AX–B<sub>2</sub>X<sub>3</sub>. A metallic mixed oxide system with the spinel and an additional compound, particularly an oxide, may also be present. The spinel, or the spinel  
10 present as a mixture, can have an oxide or several oxides of the group comprising NiO, CoO, Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>. This can be the case even if said oxides are not already a component of the spinel. In particular, said oxides can be present in an aluminate or a chromate spinel.

15 Furthermore, the spinel or a spinel consisting of a mixture can have an oxide or several oxides of the group comprising magnesium oxide (MgO), zirconium oxide (ZrO<sub>2</sub>) and hafnium oxide (HfO<sub>2</sub>). This can be the case with spinels in which the oxides MgO, ZrO<sub>2</sub> and HfO<sub>2</sub> are not already a component of the ternary system or the spinel, particularly with a chromate spinel or an aluminate spinel. A zirconium  
20 oxide or hafnium oxide present in the spinel is partially or fully stabilized particularly with yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) or another rare earth oxide. A rare earth metal is hereby understood to mean, for short, one of the elements scandium, yttrium, lanthanum, as well as the lanthanides such as cerium and ytterbium. Furthermore, oxides of the actinides may also be added.

25 The bond coat has preferably an alloy that comprises at least one element of the spinel. Hence, through at least partial oxidation of the bond coat, an oxide is formed of this element that is also contained in the spinel, e.g., aluminum, chromium, cobalt or others to provide good adhesion of the spinel to the bond coat. The bond  
30 coat is preferably an alloy of the type MCrAlY, where M represents an element or several elements of the group comprising iron, cobalt or nickel, Cr represents

- chromium, Al aluminum, and Y yttrium or a reactive rare earth element. Furthermore, the bond coat can include, e.g., 1 to 15 wt-% rhenium. The chromium content preferably ranges from 3% to 50%, particularly from 12% to 25%, the aluminum content is preferably between 3% and 20%, particularly 5 between 5% and 15%. The yttrium content is preferably between 0.01% and 0.3%.

The product is preferably a component of a thermal turbo machine, particularly a gas turbine. In particular, it is a turbine moving blade, a turbine stationary blade, or a heat shield of a combustion chamber. The metallic basic body preferably has a 10 nickel-, cobalt- and/or chromium based superalloy. It is also possible to provide a furnace or similar component with a thermal barrier coating made of a spinel.

- The advantage of the spinels is their high tolerance to impurities, e.g., due to the formation of simple or complex mixed crystals in the presence of iron, aluminum, 15 nickel, chromium or other metals, a good characterization of the sintering behavior of the high-melting spinels, and an essentially cubic structure and therefore quasi isotropic thermal expansion. Spinels furthermore exhibit good chemical resistance, high thermal shock resistance and high strength. Even with a transition of a spinel from its normal form to the inverse form, or at least partially to the inverse form, 20 there are no abrupt changes in the physical-chemical properties. The transition from normal to inverse spinel can thus be considered an order-disorder induced phase transition of the second order, which has no great influence on the properties of the thermal barrier coating.
- 25 Thermal barrier coatings with a spinel may be produced, for example, by simple plasma spraying. A thermal barrier coating with a corresponding porosity can be produced by atmospheric plasma spraying. Alternatively, the thermal barrier coating may be applied by means of vapor deposition, e.g., an electron beam PVD process, with an adjustable columnar structure.

Preferably, the thermal barrier coating is applied by atmospheric plasma spraying, particularly with a predefinable porosity. The metallic mixed oxide system may also be applied by means of a suitable vapor deposition process, a suitable PVD process (Physical Vapor Deposition), particularly a reactive PVD process. When the

- 5 thermal barrier coating is applied by means of vapor deposition, e.g., an electron beam PVD process, a columnar structure can be achieved if required. In a reactive PVD process, a reaction, particularly a conversion, of the individual components of a ternary oxide or a pseudo ternary oxide takes place only during the coating operation, particularly directly upon striking the product. In non-reactive vapor

10 deposition, the previously pre-reacted products, particularly the ternary oxides with a perovskite structure are evaporated and are then deposited from the vapor onto the product. The use of pre-reacted products is advantageous particularly if plasma spraying is used.

15 The production (synthesis) of the spinels, e.g.,  $\text{NiCr}_2\text{O}_4$ ,  $\text{NiAl}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$  can be carried out phase-shift-free in the "mixed oxide process." In this case, the starting powders used are the associated binary oxides, e.g.,  $\text{Cr}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ . These powders can be homogenized under isopropanol, cold isostatically pressed, particularly at a pressure of 625 mPa, and subsequently tempered for 50

20 hours at 1500° C in air at a heat rate of 5 K/min.

The invention will now be described in greater detail, by way of example, with reference to the drawing in which:

- 25 FIG 1 is a perspective view of a gas turbine blade and  
FIG 2 and 3 are each a segment of a cross-section through the turbine blade  
depicted in Figure 1.

- Figure 1 shows a product 1, in this case a gas turbine blade 1, with a metallic basic body 2 made of a nickel-based, cobalt-based or chromium-based superalloy. The gas turbine blade 1 has a blade root 10 for mounting to a turbine shaft (not depicted), a

- vane 9 adjoining the blade root and a seal strip 8 bordering vane 9. At least on vane 9, gas turbine blade 1 is coated with a bond coat 3 (see Figures 2 and 3) and a thermal barrier coating 4 is applied thereto. Between the thermal barrier coating 4 and the bond coat 3, an oxide layer 5 is formed having an oxide of a metallic element of the alloy of bond coat 3. The bond coat has an alloy of the MCrAlY type, where M represents an element or several elements of the group comprising iron, cobalt and nickel, Cr represents chromium, Al aluminum, and Y yttrium or a rear earth element. The thermal barrier coating 4 applied to bond coat 3 has a spinel of the structural formula  $AB_2O_4$ , particularly a 2-3 spinel. The 2-3 spinel has a metallic element B, particularly chromium or aluminum, and an additional metallic element A, particularly magnesium, nickel or cobalt, e.g.,  $MgAl_2O_4$ ,  $CoAl_2O_4$ ,  $MgCr_2O_4$ ,  $CoCr_2O_4$ , or  $TiMg_2O_4$ . A 2-3 spinel can furthermore be present as a ternary system of the actual spinel and a respective oxide of a bivalent metallic element and a trivalent metallic element. Furthermore, an additional oxide, particularly  $MgO$ ,  $ZrO_2$ ,  $HfO_2$ ,  $NiO$ ,  $CoO$ ,  $Al_2O_3$  or  $Cr_2O_3$  can be admixed to the spinel or to the spinel containing a mixture. Oxide layer 5 and bond coat 3 ensure good adhesion of the thermal barrier coating 4 to the metallic basic body 2.

- Figure 3 shows a coating system analogous to that shown in Figure 2 in which the basic body 2 is provided with a bond coat 3 to which the thermal barrier coating 4 is applied. Bond coat 3 has a rough surface, such that thermal barrier coating 4 essentially adheres to bond coat 3, and thus to basic body 2, without a chemical bond but through mechanical anchoring. This roughness of surface 11 of bond coat 3 can be provided already through the application of bond coat 3, e.g., by vacuum spraying. The thermal barrier coating 4 can also be applied directly to the metallic basic body 2 through a corresponding roughness of the metallic basic body 2. It is also possible to apply an additional bond coat between bond coat 3 and thermal barrier coating 4, e.g., with an aluminum nitride or a chromium nitride.
- 30 To ensure good and permanent adhesion, even when the product is exposed to a hot gas 7 during operation of the turbine system (not depicted), the high thermal

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- expansion coefficient of the spinel, which is close to that of the thermal coefficient of the superalloy, achieves [sic]. The fact that the spinel has low thermal conductivity, a high melting point and no critical phase transition at the temperatures of the gas turbine system, which can reach more than 1250° C on 5 surface 6 of thermal barrier coating 4, further contributes to a permanent bond. This ensures a long service life even with alternating thermal stresses of gas turbine blade 1.

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## Claims

1. High-temperature resistant component (1) of a gas turbine that can be exposed to a hot aggressive gas with a metallic basic body (2) having a bond coat (3) and a ceramic barrier coating (4) applied thereto, whereby the bond coat (3) is disposed between the basic body (2) and the ceramic thermal barrier coating (4), and whereby the ceramic thermal barrier coating (4) comprises an inner coating region facing the bond coat (3) and an outer coating region facing away from the bond coat (3), whereby the inner coating region has a spinel of the structural formula  $AB_2X_4$  and/or  $B(AB)_2X_4$ , and where

- X represents an element or several elements of the group comprising oxygen, sulfur, selenium and tellurium,
- A represents an element or several elements of the group comprising aluminum, manganese, iron, cobalt, nickel, copper, zinc, cadmium, silicon, titanium and tungsten, and
- B represents an element or several elements of the group comprising aluminum, magnesium, manganese, iron, vanadium, chromium, gallium, silicon, titanium, sodium and potassium.

2. Component (1) as claimed in Claim 1,  
characterized in that B represents aluminum (aluminate spinel) or chromium (chromium spinel), A represents nickel, cobalt or titanium, and X represents oxygen.

3. Component (1) as claimed in Claim 1,  
characterized in that B represents magnesium, A titanium, and X represents oxygen.

4. High-temperature resistant component (1) of a gas turbine that can be exposed to a hot aggressive gas with a metallic basic body (2) having a bond coat (3) and a ceramic barrier coating (4) applied thereto, whereby the bond coat (3) is disposed between the basic body (2) and the ceramic thermal barrier coating (4), and whereby the ceramic thermal

barrier coating (4) comprises an inner coating region facing the bond coat (3) and an outer coating region facing away from the bond coat (3), whereby the inner coating region has a spinel of the structural formula  $AB_2X_4$  and/or  $B(AB)_2X_4$ , characterized in that B represents aluminum (aluminate spinel) or chromium, (chromium spinel), A represents magnesium, and X represents oxygen.

5. Component (1) as claimed in one of the preceding claims, characterized in that the spinel is present as a mixture in the ternary system of the type  $AB_2X_4-AX-B_2X_3$ .

6. Component (1) as claimed in one of the preceding claims, characterized in that the mixed oxide system with the spinel has an additional oxide or several additional oxides.

7. Component (1) as claimed in one of the preceding claims, characterized in that the additional oxide is stabilized with yttrium oxide ( $Y_2O_3$ ) or another rare earth oxide.

8. Component (1) as claimed in one of the preceding claims, characterized in that between basic body (2) and thermal barrier coating (4) a bond coat (3) forming a bonding oxide is disposed.

9. Component (1) as claimed in Claim 8, characterized in that the bond coat (3) is an alloy comprising at least one of the elements of the spinel.

10. Component (1) as claimed in one of the preceding claims, characterized in that it is designed as a turbine moving blade, a turbine stationary blade or a heat shield of a combustion chamber.

11. Component (I) as claimed in one of the preceding claims,  
characterized in that the thermal expansion coefficient  $\alpha$  of the spinel is between  $6 \cdot 10^{-6}$ /K and  $17 \cdot 10^{-6}$ /K.

12. Component (1) as claimed in one of the preceding claims,  
characterized in that the thermal conductivity of the spinel is between 1.0 W/mK and  
4.0 W/mK

13. Component (1) as claimed in one of the preceding claims, wherein the metallic basic body (4) has a nickel-, cobalt- and/or chromium-based super alloy.

14. Process for producing a thermal barrier coating (4) on a component (1) of a gas turbine with a metallic basic body that has a bond coat (3) applied thereto, wherein a spinel of the structural formula  $AB\text{-}X_2$  and/or  $B\text{-}(AB)_2\text{-}X_4$ , where

- X represents an element or several elements of the group comprising oxygen, sulfur, selenium and tellurium,
  - A represents an element or several elements of the group comprising aluminum, manganese, iron, cobalt, nickel, copper, zinc, cadmium, silicon, titanium and tungsten, and
  - B represents an element or several elements of the group comprising aluminum, magnesium, manganese, iron, vanadium, chromium, gallium, silicon, titanium, sodium and potassium, is applied to the component (1) by plasma spraying or by vapor deposition.

### Abstract

Product, Particularly a Gas Turbine Component, with Ceramic Thermal Barrier  
5 Coating

The invention relates to a product (1), particularly a gas turbine blade that can be  
exposed to a hot aggressive gas (7). The product (1) has a metallic basic body (2)  
which is provided with a thermal barrier coating (4) having a spinel of the  
10 composition  $AB_2O_4$ .

FIG 2

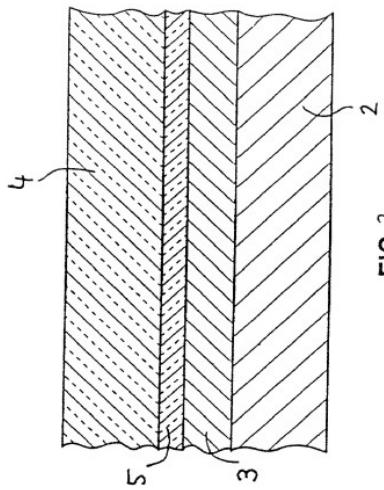


FIG 2

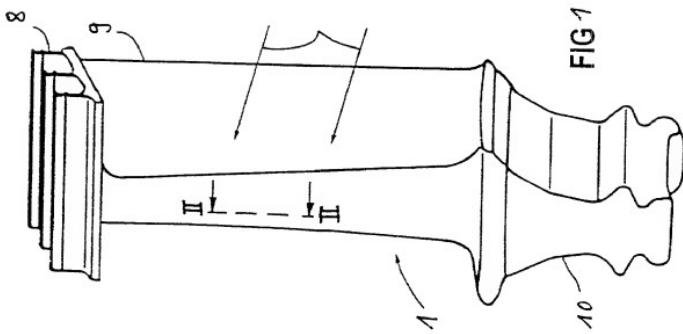
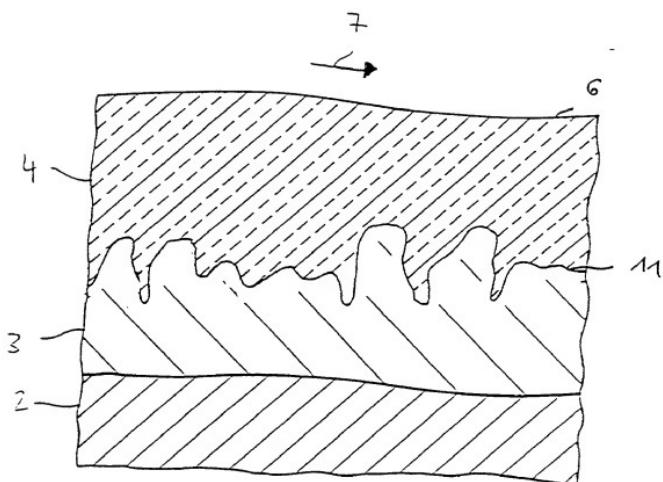


FIG 1

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**DECLARATION FOR UTILITY OR  
DESIGN  
PATENT APPLICATION  
(37 CFR 1.63)**

Declaration Submitted with Initial Filing       Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)

Attorney Docket Number	97P 8646
First Named Inventor	Beate Heimberg
COMPLETE IF KNOWN	
Application Number	09 / 530,653
Filing Date	May 3, 2000
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled,

**Product, particularly component of a gas turbine,  
with ceramic thermal barrier coating**

the specification of which

(Title of the Invention)

is attached hereto

OR

was filed on (MM/DD/YYYY) **11/03/98**

as United States Application Number or PCT International

Application Number **PCT/US98/03207** and was amended on (MM/DD/YYYY) **12/99 & 01/00** if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?
19748537.5	DE	11/03/97	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input checked="" type="checkbox"/> <input type="checkbox"/>

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[Page 1 of 2]

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PCT/US98/03207	11/03/98	

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Name of Sole or First Inventor:	<input type="checkbox"/> A petition has been filed for this unsigned inventor		
Given Name (first and middle if any!) <u>Beate</u>		Family Name or Surname <u>Heimberg</u>	
Inventor's Signature	<u>Beate Heimberg</u>		Date 25/05/00
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Post Office Address			
City	Mulheim a.d.Ruhr	State	ZIP D-45478
Country	DE		

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		Page <u>1</u> of <u>4</u>

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Inventor's Signature						Date <u>06-08-2000</u>
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Post Office Address	An der Schinnenburg 28					
Post Office Address						
City	<u>Ratingen</u>	State	ZIP	D-40883	Country	DE
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Given Name (first and middle [if any])		Family Name or Surname				
<u>Ulrich</u>		<u>Bast</u>				
Inventor's Signature						Date <u>29/06/2000</u>
Residence: City	<u>Munchen</u>	State	Country	DE	DEX	Citizenship
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Given Name (first and middle [if any])		Family Name or Surname				
Inventor's Signature	<u>Thomas Haubold</u>			Date	28/11/00	
Residence: City	WEHRHEIM Weinheim	State	Country	DE DEX	Citizenship	
Post Office Address	Hilde-Coppi-Str. 18					
Post Office Address						
City	WEHRHEIM Weinheim	State	ZIP	D-61273	Country	DE
<b>Name of Additional Joint Inventor, if any:</b>		<input type="checkbox"/> A petition has been filed for this unsigned inventor				
Given Name (first and middle [if any])		Family Name or Surname				
Inventor's Signature	<u>Michael Hoffmann</u>			Date		
Residence: City	Ettlingen BÖTTLINGEN	State	Country	DE DEX	Citizenship	
Post Office Address	Streuerweg 18 Erikerstr. 26 <u>Michael Hoffmann 21.11.2000</u>					
Post Office Address						
City	Ettlingen	State	ZIP	76275 D-71092	Country	DE
<b>Name of Additional Joint Inventor, if any:</b>		<input type="checkbox"/> A petition has been filed for this unsigned inventor				
Given Name (first and middle [if any])		Family Name or Surname				
Inventor's Signature	<u>Axel Endriss</u>			Date	21/05/00	
Residence: City	Stuttgart Karlsruhe	State	Country	DE DEX	Citizenship	
Post Office Address	Scheffelplatz 1 Flamingoweg 68 <u>Axel Endriss, 21/05/2000</u>					
Post Office Address						
City	Stuttgart Karlsruhe	State	ZIP	D-70378 D-70133	Country	DE

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Please type a plus sign (+) inside this box → DECLARATION ADDITIONAL INVENTOR(S)  
Supplemental Sheet  
Page 3 of 4Name of Additional Joint Inventor, if any:  A petition has been filed for this unsigned inventorGiven Name (first and middle [if any]) Family Name or Surname  
Peter GreilInventor's Signature Peter Greil Date 04.07.00  
Residence: City Weisendorf State  Country DE Citizenship DEXPost Office Address Am Hochstock 27Post Office Address City Weisendorf State  ZIP D-91085 Country DEName of Additional Joint Inventor, if any:  A petition has been filed for this unsigned inventorGiven Name (first and middle [if any]) Family Name or Surname  
Chu-Wan HongInventor's Signature Chu-Wan Hong Date 02.10.00  
Residence: City Stainz State Kirchhrenbach Country DE Citizenship AT HTXPost Office Address Ahornweg 15- Stallhof 23Post Office Address City Stainz State Kirchhrenbach ZIP D-91350 Country ATName of Additional Joint Inventor, if any:  A petition has been filed for this unsigned inventorGiven Name (first and middle [if any]) Family Name or Surname  
Fritz AldingerInventor's Signature Fritz Aldinger Date 18.08.00  
Residence: City Leinfelden-Echingen State  Country DE Citizenship DEXPost Office Address Waldstr. 20Post Office Address City Leinfelden-Echingen State  ZIP D-70771 Country DE

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<b>DECLARATION</b>		<b>ADDITIONAL INVENTOR(S) Supplemental Sheet</b>
		Page <u>4</u> of <u>4</u>

<b>Name of Additional Joint Inventor, if any:</b>		<input type="checkbox"/> A petition has been filed for this unsigned inventor				
Given Name (first and middle [if any])		Family Name or Surname				
Hans J.		Seifert				
Inventor's Signature	<i>Hans J. Seifert</i>				Date	11/03/00
Residence: City	Stuttgart	State		Country	DE	DEX
Post Office Address	Zamenhofstr. 56 new: Fleckenwaldweg 6 Hans J. Seifert					
Post Office Address						
City	Stuttgart	State		ZIP	D-70195	Country
				ZIP	D-70197	Country
<b>Name of Additional Joint Inventor, if any:</b>		<input type="checkbox"/> A petition has been filed for this unsigned inventor				
Given Name (first and middle [if any])		Family Name or Surname				
Inventor's Signature					Date	
Residence: City		State		Country	Citizenship	
Post Office Address						
Post Office Address						
City		State		ZIP		Country
<b>Name of Additional Joint Inventor, if any:</b>		<input type="checkbox"/> A petition has been filed for this unsigned inventor				
Given Name (first and middle [if any])		Family Name or Surname				
Inventor's Signature					Date	
Residence: City		State		Country	Citizenship	
Post Office Address						
Post Office Address						
City		State		ZIP		Country

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DECLARATION		REGISTERED PRACTITIONER INFORMATION (Supplemental Sheet)	
Name	Registration Number	Name	Registration Number
Daniel C. Abeles	25,822	Darryl A. Smith	37,723
Brij K. Agarwal	43,507	Daniel J. Staudt	34,733
Adel A. Ahmed	29,606	Erik C. Swanson	40,194
Debra Z. Anderson	44,506	Alan G. Towner	32,949
I. Marc Asperas	37,274	Heather S. Vance	39,033
Stanton C. Braden	32,556	Michael J. Wallace, Jr.	44,486
Robert T. Canavan	37,592	Scott T. Weingaertner	37,756
Dexter K. Chin	38,842	Russell C. Wells	24,188
Daniel P. Cillo	25,108	Richard V. Westerhoff	24,454
Joseph S. Codispoti	31,819	Jeffrey S. Whittle	36,382
Kirk D. Houser	37,357	Ira Lee Zebrazk	31,147
Tracy Lynn Hurt	34,188		
Mark H. Jay	27,507		
Stuart Kaler	35,913		
Rosa S. Kim	39,728		
David C. Jenkins	42,691		
William F. Lang IV	41,928		
Robert P. Lenart	30,654		
Peter A. Luccarelli, Jr.	29,750		
David Maire	34,865		
James Markarian	31,277		
Diane R. Meyers	38,968		
Jeffrey P. Morris	25,307		
Pasquale Mussachio	36,876		
John P. Musone	44,961		
Carl Napolitano	37,405		
Donald B. Paschburg	33,753		
Clifford A. Pastel	46,013		
David V. Radack	33,442		
Arnold B. Silverman	22,614		
Laura M. Sienzak	35,363		

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